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Direct correlation of surface morphology with electron emission sites for intrinsic nanocrystalline diamond films

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Abstract

Field emission properties of nanocrystalline diamond films show low turn-on fields resulting in significant electron emission at low applied fields originating from individual sites with an emission site density of $\sim 10^4/\text{cm}^2$. We have employed a high resolution electron emission microscope operating in field emission mode to image the spatial distribution of emission sites for intrinsic nanocrystalline diamond thin films. The location of individual emission sites has been directly correlated to the surface morphology probed by scanning electron microscopy. Surface topography measurements show fine structured features consisting of micron and submicron domains separated by grain boundaries. No preferred topographic features that would account for field emission can be detected suggesting that the electronic structure of the grains and their boundaries under a high electric field has to be considered in order to account for the observed emission characteristics.

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1. Introduction

Carbon based materials, i.e. diamond, nanocrystalline diamond as well as carbon nanotubes (CNT's) exhibit a distinct and characteristic electron emission behavior with its origin still widely discussed. Diamond and, in particular, doped diamond, have been shown to exhibit minimal field emission at room temperature but at elevated temperature a uniform emission component is observed [1]. Nanocrystalline carbon films, in general, display electron emission from nanometer sized sites with a temperature dependence that is affected by doping [2]. Attempts were made to explain this singular emission behavior by establishing a 'field enhancement' map, $\beta(x, y)$ that would account for site emission due to local changes in the topographic field enhancement. However, the observed field enhancement due to film morphology could not account for the observed emission characteristic [3-6]. In this article we present a technique to directly correlate electron emission from singular emission sites with the morphology of nanocrystalline diamond films.

2. Experimental procedure

Nanocrystalline diamond films were synthesized by microwave plasma assisted chemical vapor deposition (MPCVD). The films were grown on low resistivity (< 1 Ω cm) Si(100) after ultrasonic surface pretreatment in an ethanol/diamond/titanium suspension for nucleation enhancement. The process gases were zero grade hydrogen and methane. Growth conditions were as follows: flow rates of 180 sccm hydrogen and 20 sccm methane, 20 Torr chamber pressure, 900 W microwave power, and substrate temperature of 900 °C.

The samples were characterized using Raman spectroscopy with an excitation of 514.5 nm. Electron emission measurements were performed with an electron emission microscope, which can be operated in different modes. Field emission measurements were conducted by applying an electric field up to 5 V/ μ m, which was obtained with a voltage of 20 kV over the sample-anode distance of 4 mm. With this setting the instrument can be employed to record real time images of the sample surface and thus map the electron emission with a lateral resolution of ~10 nm. Utilizing UV light from a mercury arc lamp enables photo-electron emission microscopy (PEEM) to image the surface topography. Scanning electron microscopy (SEM) was utilized to

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Fig. 1. Field-electron emission microscopy (FEEM) of a region of intrinsic nanocrystalline diamond showing five emission sites.

image surface topography with higher resolution. Imaging the distinct arrangement of emission sites by field emission microscopy and surface features by photoelectron emission microscopy allows the correlation of individual emitting sites with the sample morphology as imaged by scanning electron microscopy.

3. Results and discussion

Electron emission microscopy in contrast to other field emission measurement techniques is a non-scanning process which enables real time observation of surface processes. Applying an electric field between the sample surface and the perforated anode ensures a nearly uniform field distribution over the imaged sample area. The macroscopic field is thus the anode voltage over the sample-anode spacing.

Field emission maps of several hundreds of microns can be acquired as shown in Fig. 1, which depicts an electron emission pattern of a nanocrystalline diamond film under an electric field of 5 V/ μ m.

With the above emission pattern an emission site density of approximately 10^3-10^4 sites/cm² is deduced. In order to account for the observed emission behavior, field emission considerations would suggest these emis-

sion sites to be significantly different from their surrounding area, i.e. singular emission from a site induced by a high local topographic field enhancement. It has been argued that high field enhancement factors of submicron surface protrusions are responsible for localized electron emission [7]. High local field enhancement would allow electrons to be emitted into vacuum corresponding to Fowler-Nordheim emission. With this in mind we have been led to consider scanning electron microscopy to investigate the surface morphology and thus locate sites that exhibit high field enhancement. Fig. 2 shows electron emission micrographs and a corresponding scanning electron micrograph of a region of a nanocrystalline diamond film with a single emission site. The boxes in each image correspond to the same surface area. This film consists of submicron grains, which are presumed to be separated by sp^2 carbon boundaries. We note that the box in Fig. 2 indicates the location of the only emission site observed in the whole imaged area.

Scanning electron microscopy has been employed to image the microscopic structure of a nanocrystalline diamond film as is shown in Fig. 3. The sample surface exhibits this type of microstructure uniformly over the film with no identifiable topographically preferred loca-



Fig. 2. Scanning electron micrograph of a nanocrystalline diamond film with one emission site located within the indicated box. (a) shows the photo-electron emission (PEEM) image; (b) the field emission (FEEM) and (c) the scanning electron micrograph.



Fig. 3. Scanning electron micrograph of a nanocrystalline sample surface showing the microstructure without any emission site present.

tions, indicating a uniform distribution for the corresponding field enhancement. Topographic field enhancement can arise from surface protrusions as well as indentations, which are imaged in Fig. 3. However, our measurements do not indicate that unusual sharp structures correspond to emission sites.

It has also been argued that electron emission occurs at grain boundaries that supply a conductive matrix through which carriers can be transported. An increase in the grain boundary density as observed for nanocrystalline diamond films grown with a decrease of the hydrogen gas flow ratio, which has been shown to exhibit an increase in the emission site density [8]. However, the uniform and high density distribution of grains and boundaries does not account for the observed low density of active sites that exhibit field emission. These experimental results confirm the shortcomings of the topographic field enhancement argument to explain this emission behavior. It appears that the electronic structure of nanocrystalline diamond should be considered as an additional contribution to field emission.

The electronic states of disordered or nanocrystalline diamond is significantly affected by the variation in the bonding. The sp² bonded regions will directly contribute states in diamond band gap. Distortions of the sp³ bonded sites can also contribute states in the gap. Furthermore, impurity atoms such as N or O, which are commonly present during growth, can alter the electronic structure [9]. These contributions to the electronic structure can give rise to a change in the local emissivity resulting in localized emission.

We now consider differences in the PEEM and FEEM images of the nanocrystalline diamond surfaces. Fig. 2a depicts the PEEM image of a nanocrystalline diamond film acquired with UV light from a mercury arc lamp. The difference in the lateral size of the emission site in the PEEM and field emission images can be attributed to a brightness change due to a contribution from photoexcited electrons and possibly a change in the focal length of the emission site. The electron emission microscope forms an image from objects in a focal plane without any focal depth, i.e. objects above or below the focal plane will be blurred and out of focus. The focal length is determined by the electron optics parameters (lens currents) and the energy of the electrons. The scanning electron micrograph in Fig. 2c does not exhibit any significant surface protrusions that would cause an emission site to be out of focus in electron emission microscopy. We have found that there is often a difference in the focal conditions of PEEM and FEEM images of the same region of the surface. Focused PEEM images result in blurred emission sites as is shown in Figs. 2a and 4a. Increasing the lens current results in focused emission sites (Figs. 2b and 4b). This increase of the lens current corresponds to an increased energy of the electrons originating from the emission site compared to electrons emitted from the surrounding area, which is an indication of the energy difference of electrons emitted from different regions of the sample surface.

This change in energy of the emitted electrons suggests that the local electronic structure of the emission sites is different from the surrounding regions. We have found that a decrease of the accelerating voltage will bring the emission site back into focus. The exact mechanism that causes this energy discrepancy is currently under investigation. The energy difference of the emitted electrons from the emission sites and surroundings may be the result of an unusual field distribution at the location of emission. Another important parameter is the exact electronic structure of the emission site, which is still widely debated.

4. Conclusions

Nanocrystalline diamond films with their characteristic grain structure embedded into a grain boundary matrix exhibit emission from singular sites. Correlating emission sites detected by electron emission microscopy



Fig. 4. Field emission microscopy of a single emission site on a nanocrystalline diamond film surface, with the focal plane in (a) on the surface and in (b) on the emission site indicating a change in energy of the field and photo emitted electrons.

with surface morphology from scanning electron microscopy indicates no correspondence of emission sites and topography. This indicates that topographic field enhancement can not be the sole origin of the emission characteristics. The variations in bonding in the nanocrystalline films including sp^2 bonded sites, distorted sp^3 bonded sites, and impurities will cause a change in the local density of electronic states, which may correspond to regions of a preferred band configuration that exhibits the observed emission behavior.

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